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HYDROGEN OVERVOLTAGE

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Hydrogen overvoltage may be defined as the difference of potential that exists between a reversible hydrogen electrode, and an electrode, in the same solution, at which hydrogen, H_2 , is being formed from hydrogen ions. A reversible hydrogen electrode is one at which the reaction



(ϵ = electron) has reached equilibrium. This equilibrium is attained, and maintained, during the passage of very small currents, only on electrodes covered with a dispersed 'noble' metal, such as platinum. If stronger currents are passed across such a metal-electrolyte boundary, or if other electrodes are used, the reaction does not take place under equilibrium conditions and an overvoltage appears. For instance, it requires an overvoltage of about 0.2 volt to liberate hydrogen gas from a polished platinum surface, and about 0.7 volt from a lead surface.

On attempting to determine the overvoltage of small electrodes of 'platinized' platinum the authors observed some interesting fluctuations in the measured voltage, a typical series of measurements being plotted in figure 1. Here ordinates represent overvoltage in millivolts and abscissae time in seconds. Bubbles were evolved at the points marked by small circles, there being one bubble to each fluctuation. At the low current densities used, the bubbles came off at a single point on the electrode, making it appear probable that the nucleus of the next bubble remained on the electrode after each bubble had separated.

When Reaction 1 takes place it is probable that the greater part of the liberated hydrogen goes directly into solution. Unless carried away by diffusion, stirring, or other means, the concentration of dissolved hydrogen, in immediate contact with the electrode, will tend to rise and produce a supersaturated solution. It is this layer of dissolved hydrogen that is responsible for the overvoltage. However, if there is a nucleus of *gaseous* hydrogen on the electrode a portion of the liberated hydrogen will enter this gaseous phase. A gaseous nucleus will thus play a similar rôle to that of a small crystal in a supersaturated salt solution. It is evident that hydrogen gas in the form of small bubbles must have a larger energy content, per mol of gas, than the same volume of undispersed gas, as energy must be expended in overcoming the surface tension in the formation of the bubbles. Such bubbles will be more soluble (i.e., remain at equilibrium with more concentrated dissolved hydrogen) than the undispersed gas. This is analogous to

the increase of solubility produced by the fine grinding of solids. An electrode in equilibrium with small bubbles will thus reach a higher potential than one in contact with undispersed gas.

With the foregoing in mind we can proceed to an explanation of the voltage fluctuations. At *a* (fig. 1) a bubble has separated from the electrode, leaving a nucleus behind. As the electrolysis proceeds this nucleus will grow, obtaining hydrogen from the supersaturated solution or from the electrode. However, as the nucleus increases in size, the energy necessary to produce further increases in volume must decrease, as the ratio

$$\frac{\text{increase in surface}}{\text{increase in volume}}$$

is continuously decreasing. If the bubble is growing slowly the hydrogen bearing solution surrounding the electrode will tend to get into equilibrium with the bubble. This accounts for the decrease in overvoltage from *a* to *b*.

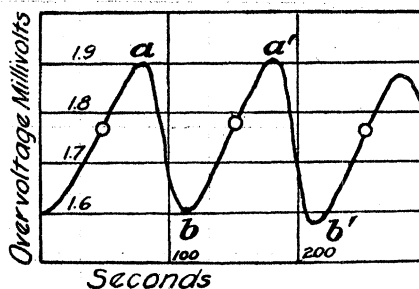


FIG. 1

At *b* the buoyant effect of the electrolyte is sufficient to overcome the attraction of the electrode for the bubble, which breaks away, leaving a nucleus behind. Bubbles are, however, seldom observed to come off at points corresponding to *b*; they probably remain in the pores of the electrode, and are pushed out by the growth of the following bubble. From *b* to *a'* the concentration of dissolved hydrogen is increasing to a value such that the nucleus can again grow, when the processes described above are repeated.

It is evident that it makes no difference, in so far as the absorption of energy is concerned, whether small bubbles are evolved, or a solution of hydrogen in equilibrium with the bubbles is formed. In the following paragraph it is assumed that all the hydrogen is liberated as bubbles.

The number of bubbles of radius *r* that can be formed from a mol of hydrogen of volume *V* is $3V/4\pi r^3$. To obtain the surface energy of such a system this must be multiplied by $4\pi r^2$ and the surface tension γ . Substituting RT/p for *V* (*R*, *T* and *p* are the gas constant, the absolute temperature and the pressure respectively) and equating the surface energy with the electrical

energy, $2FE$, in which F is the Faraday equivalent and E the overvoltage, we obtain:

$$2FE = \frac{4\pi r^2 RT}{4/3\pi r^3 p} \gamma = \frac{3RT}{pr} \gamma \quad (2)$$

Substituting 75.6 dynes per sq. cm. for γ and appropriate values for the other terms, equation 4 becomes, for 25°C. and one atmosphere

$$E = \frac{2.87 \times 10^{-2}}{4} \quad (3)$$

For platinized platinum electrodes this relation was found to hold quantitatively. For instance, in one experiment the bubbles were found to have

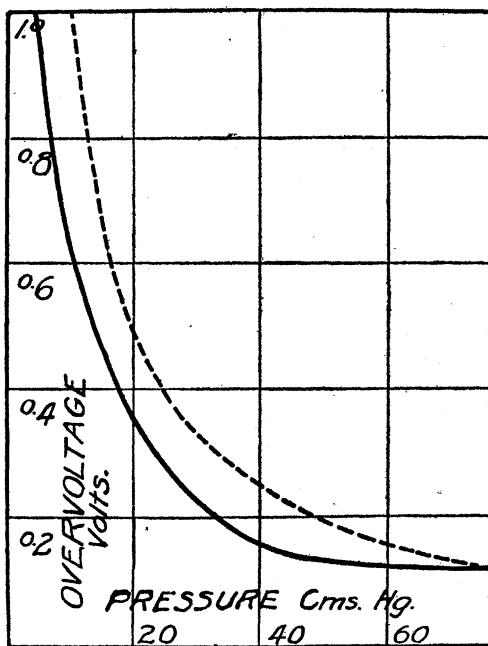


FIG. 2

radii of 0.017 mm., corresponding to an overvoltage of 1.6 mv. The observed values fluctuated between 1.9 and 1.6 mv. the latter potential, according to the theory, being that corresponding to the fully formed bubble. For electrodes of other metals difficulty was encountered in measuring the bubbles, but they were found to be smaller than those for platinized platinum in all cases observed.

If the bubble radius does not change with the pressure (as was found to be the case, up to 16 atm. pressure, with platinized platinum electrodes) the overvoltage (according to equation 2) should increase as the pressure decreases, and *vice versa*. This prediction was found to be verified in some

unpublished work by Goodwin and Wilson of the Massachusetts Institute of Technology. In figure 2 the solid line shows the experimentally determined variation with the pressure of the overvoltage of nickel. Similar curves were found for mercury and lead. The dotted line shows the variation as calculated by Equation 2, using the overvoltage at one atmosphere as a basis for computing the values for the other pressures. The difference between these two curves may be explained by an increase of stirring at the lower pressures, since many more bubbles are produced per mol of gas.

It appears quite probable, then, that the factor that determines the overvoltage of an electrode at any one pressure is the size of the gaseous nuclei that can cling to it. A number of observers have called attention to the fact that electrodes with low overvoltages are those that have large adsorptive powers. This adsorptive power is undoubtedly related to the attraction of an electrode for a gaseous nucleus.

AN APPROXIMATE LAW OF ENERGY DISTRIBUTION IN THE GENERAL X-RAY SPECTRUM

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In the spectra of X-rays as ordinarily determined there are factors of absorption in the anticathode, the glass of the tube, the reflecting crystal and the ionized gas, and of efficiency of reflection that are all functions of the frequency. Fortunately, except at the discontinuities of any of these absorptions, the unknown factors vary continuously with frequency, so that the measured intensities in the spectrum represent the energy distribution qualitatively, but by no means quantitatively. The problem of the present paper is to combine other available data in such a way as to find an approximate law of energy distribution, not involving unknown absorption factors, and avoiding also any *a priori* assumptions about the emitting mechanism. The data are incomplete and this work is merely a first approximation.

For data we have (a) some graphs of intensity against potential at constant frequency (where the unknown factors are all constant in each graph), and (b) the total energy measurements by Beatty,¹ who made the absorption negligible by using a thin window and no crystal. Some of the intensity-potential graphs were obtained in the course of experiments for another purpose with a rhodium target by the author,² and with platinum by the author and Dr. H. Clark,³ and others were obtained by taking points at the same wave length from intensity-wave length graphs drawn for tungsten by A. W. Hull,⁴ Hull and Rice⁵ and Ulrey,⁶ and for molybdenum by Hull.

In the experiments on rhodium and platinum, the spectrometer was kept at a fixed wave length and the potential was changed between readings.